

PROBING REDOX REACTIONS AT A SYNCHROTRON: THE COORDINATION ENVIRONMENT OF Np(VII)

Can one stabilize a heptavalent neptunium ion? What would be the coordination of such an ion? These questions can only be addressed with the unique opportunity to measure freshly prepared samples and to manipulate the samples, via either electrochemical or chemical means, in an x-ray beam during data collection. This capability is critical to obtaining data from valence-pure samples, as clearly demonstrated from the XANES measurements presented here on Np(VII).

Neptunium (Np, $Z = 93$) is a radioactive element that is a by-product in nuclear reactors. It is the most problematic of the 5f actinide elements for waste storage because of the projected dose commitments to the public in the event of a containment breach. Complicating this problem is the high solubility of Np in groundwater and its complex environmental chemistry, which hampers a predictive understanding of its fate and transport. Although considerable efforts have been expended to understand the solution chemistry of Np, limiting speciation data are not always available.

The complex chemistry of Np manifests itself in the dependence on Eh and pH of the relative stabilities between different oxidation states and coordination environments. For example, Np(VII) has been reported to form in highly alkaline conditions under a strongly oxidizing environment. Although it was first reported in 1967 [1], the coordination environment of Np(VII) has remained controversial, in part because of the technical difficulties associated with forming and stabilizing the highly charged ion. We have taken advantage of our recent development of *in situ* spectroelectrochemistry methodology [2], which permits the generation of Np(VII), both electrochemically and via ozone oxidation of Np(V), and the measurement of x-ray absorption spectra while controlling the redox environment. The advantages of *in situ* valence control include:

(1) The use of a single sample that remains in the beam during data collection, thereby minimizing systematic errors. (2) The same solution constituents can be used (there is no need to add stabilizing ions, such as Cl^- , to preserve an oxidation state in solution). (3) Intermediate species can be generated and analyzed to verify that the reaction has occurred [3]. The major obstacle to the formation and maintenance of Np(VII) is the necessity to prepare fresh solutions and to measure them as quickly as possible. For radioactive samples, this can be an insurmountable obstacle. However, the juxtaposition of the Advanced Photon Source and hot-chemistry laboratories on the same U.S. Department of Energy site provides us with the unique opportunity to perform such chemistry experiments in the x-ray beam, through the use of the Actinide Facility [4].

X-ray absorption spectroscopy (XAS) data were collected at the Np L_3 -edge on the BESSRC-CAT beamline 12-BM-B. The energy was calibrated by setting the inflection point of the first derivative from the Zr K-edge to 17,998 eV. Fluorescence data were collected using a nine-element Ge detector (Canberra). Data analyses were carried out following standard procedures [5,6].

The x-ray absorption near-edge structure (XANES) data obtained from a 6.5 mM Np solution, held in the x-ray beam during and after the initial production of Np(VII), either via ozonolysis or by

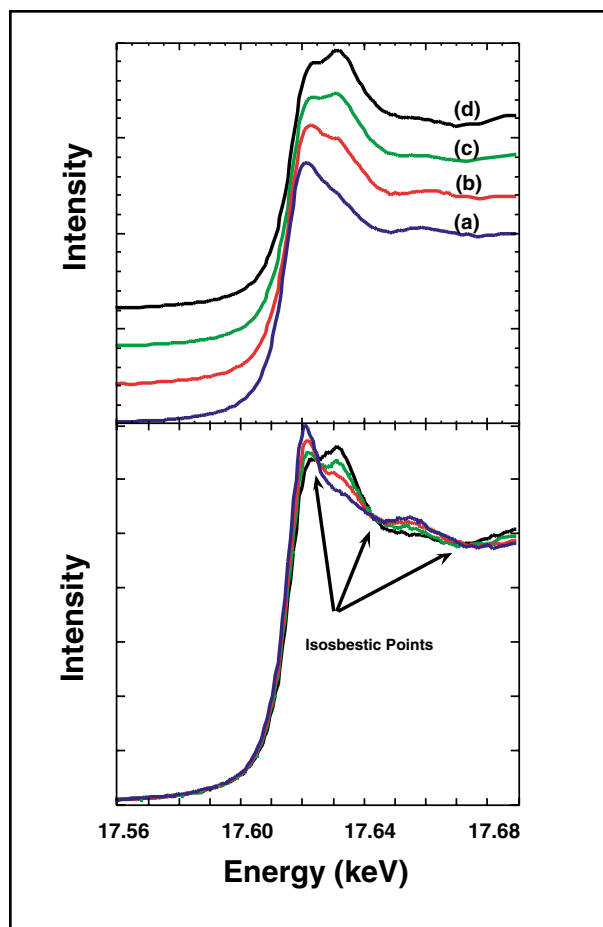


FIG. 1. Top: In situ Np L_3 -edge XANES. (a) A Np(VI) solution in 1M NaOH, after oxidation to Np(VII), held at an applied potential of +0.20 V during data collection. (b and c) Spectra of mixtures of Np(VI) and Np(VII). The data were obtained under applied potential after bulk electrolyses at intermediate potentials. (d) Spectrum of fully oxidized Np(VII). Bottom: Superimposed spectra as in top panel to indicate the presence of isosbestic points.

electrochemical generation [6], are shown in Fig. 1. The Np(VI) XANES spectrum, shown in Fig. 1a, has the high-energy shoulder that is attributable to multiple scattering from the dioxo moiety [7]. This shoulder, at approximately 17,632 eV, is enhanced significantly as the Np is oxidized, such that it has a higher intensity than the resonant peak for the Np(VII) solution and appears as a doubled white line in Fig. 1(d). The significant change in the XANES spectra with Np oxidation suggests that the coordination environment is changing.

A change in coordination environment as Np(VI) is oxidized is confirmed by analyses of the

extended x-ray absorption fine structure (EXAFS) data, shown in Fig. 2. Analysis of the Np(VI) data reveals a coordination of 2 oxygens at 1.82(2) Å and a more distant equatorial shell of 4(1) oxo (or hydroxo) ions at 2.21(3) Å. These bond distances are different than those observed for Np(VI) in acidic solution [3]. In contrast to the Np(VI) environment, the Np(VII) ion is coordinated to 4(1) oxygens at a short distance of 1.87(1) Å and 2 oxo (or hydroxo) ions at a distance of 2.24(4) Å. Therefore, although the overall coordination number and distances are similar for Np(VI) and Np(VII), the latter has four short oxygen distances, thereby forming a tetraoxo coordination. This coordination environment has been previously reported for Np(VII) in the solid state [8].

The tetraoxo coordination environment of Np(VII) that is determined from these studies is unique. It is different from the tetrahedral coordination observed for high-valent transition-metal anions or other high-valent actinide ions, which exhibit the dioxo coordination. The Np(VII) tetraoxo environment appears to result from a competition for ligand electron density that occurs between the Np d- and f-orbitals. Increased nuclear charge is expected to stabilize the 5f-orbitals with respect to the 6d-orbitals [6]. Density functional theory (DFT) calculations show that square-planar is favored over tetrahedral geometry because of increased f-orbital participation in bonding with the oxygen p-states. The DFT calculations [6] predict a slightly distorted square-planar geometry for the tetraoxo ions. This distortion allows a slightly higher Mulliken population of the d-states for D_{2h} symmetry over the D_{4h} expected from a square-planar coordination. The competition between nearly degenerate f- and d-orbitals for electron density appears to be playing a crucial role in the bonding geometry. Preliminary *in situ* spectroelectrochemical results indicate that a similar situation is found for a solution containing Pu(VII).

Whereas there have been other attempts to obtain XAS data on Np(VII) and Pu(VII) in solution, they have been unsuccessful because of the need to prepare the solutions in specially designed hot laboratories and to seal them for shipment to the

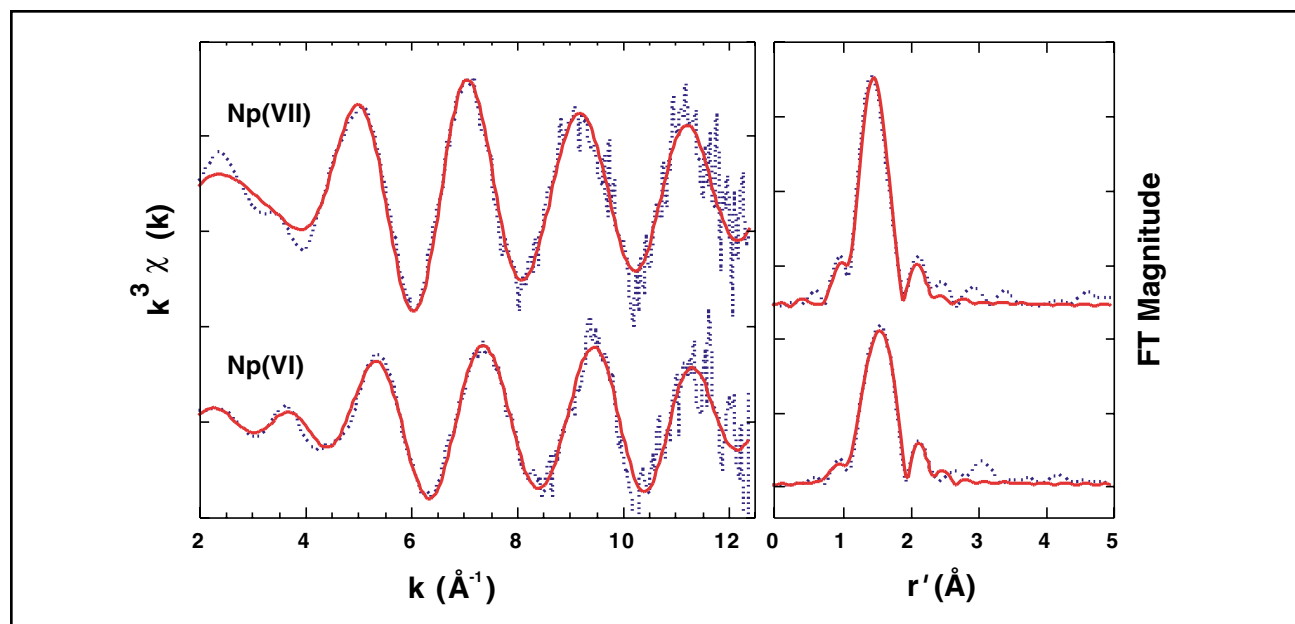


FIG. 2. Left: The k^3 -weighted EXAFS of Np(VI) and Np(VII) from experiment (blue) compared with best fit (red). Right: Fourier transform of EXAFS, uncorrected for phase shift. The unresolved peak at about 2.1 Å in the uncorrected Fourier transform is attributed to 1 to 2 Na atoms, which form a strong ion pair with the Np-O complex.

synchrotron facility, sometimes necessitating several days between sample preparation and data acquisition. The Actinide Facility affords the unique opportunity to measure freshly prepared samples and to manipulate the samples, via either electrochemical or chemical means, in the x-ray beam during data collection. This capability is critical to obtaining data from valence-pure samples, as clearly demonstrated by the work presented here on Np(VII).

This work is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract No. W-31-109-ENG-38.

Principal publication: "The Coordination Geometry of Np(VII) in Alkaline Solution," J. Amer. Chem. Soc. **123**, 4346-4347 (2001).

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